

EPA/DOE

MINE WASTE TECHNOLOGY PROGRAM

TECHNOLOGY TESTING FOR TOMORROW'S SOLUTIONS



**ANNUAL REPORT
1996**

EPA DOE Montana Tech Implemented by MSE, Inc.

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Mine Waste Technology Program
Interagency Agreement Management Committee
IAG ID NO. DW89935117-01-0

Prepared for:

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Contract No. DE-AC22-96EW96405

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PROGRAM MANAGER'S EXECUTIVE SUMMARY

The Mine Waste Technology Program (MWTP) Annual Report for Fiscal Year (FY)1996 summarizes the results and accomplishments for the various activities within the Program. After five years, everyone involved with the MWTP can look with pride to the Program's success. The MWTP has met its goals by providing assistance to the public and forming cooperative teams drawn from Government, industry, and private citizens. The funds expended have returned tangible results, providing tools for those faced with mine waste remediation challenges.

Through Montana Tech of the University of Montana (Montana Tech), a computer system was established that allows for immediate and centralized access to world-wide mineral- and mining-related information data bases. Montana Tech also established a post-graduate degree program with a mine waste emphasis in which 21 students are presently enrolled. The quality of short courses offered by Montana Tech is becoming highly recognized among the mine waste remediation community.

Technology development has proceeded successfully through the efforts of Montana Tech and MSE Technology Applications, Inc. (MSE). Six bench-scale research projects are underway at Montana Tech and are attracting interest from industry.

The three on-going MSE field demonstrations and the three developed in FY96 included participation by mine owners and mining companies, the Federal Government, and involved stakeholders. The necessary liability agreements, access agreements, National Environmental Policy Act requirements, and State of Montana and Federal permitting were all addressed.

Wide support for the MWTP is evidenced by the Program's success to date. Good working relationships have been established with the U.S. Environmental Protection Agency; U.S. Department of Energy; U.S. Department of the Interior, Bureau of Land Management; U.S. Department of Agriculture, Forest Service; Montana Bureau of Mines and Geology; Montana Department of State Lands; Montana Department of Health and Environmental Quality; Nevada Department of Conservation and Natural Resources; Northern Plains Resource Council; Montana Environmental Information Center; Clark Fork-Pend Oreille Coalition; Atlantic Richfield Company; ASARCO; Pegasus Gold; Echo Bay Minerals Company; Montana Power Company; Montana Resources; Noranda; TVX Gold; Homestake Mining; Montana Gold Ventures; Crystal Mine owners; National Mining Association; Western Governors' Association; the national laboratories; and numerous mining associations and state associations.

The MWTP recognizes its major accomplishments and looks forward to providing new and innovative technologies; meeting the challenges of mine waste remediation; and providing low cost, permanent solutions to the nation's mineral waste problems.

Creighton Barry
MSE MWTP Program Manager

INTRODUCTION

Mining waste generated by active and inactive mining production facilities and its impact on human health and the environment are a growing problem for Government entities, private industry, and the general public. The nation's reported volume of mine waste is immense. Presently, there are 68 sites on the Environmental Protection Agency's (EPA) National Priorities List.

Environmental impacts associated with inactive and abandoned mines (IAMs) are common to mining districts around the country. A recent scoping study conducted by the Western Governors' Association Mine Waste Task Force identified the following IAM statistics:

- Montana—over 20,000 IAM sites covering 153,800 acres, with 1,118 miles of stream damage;
- Arizona—80,000 IAM sites covering 136,653 acres, polluting 200 miles of surface waterways;
- Missouri—7,655 IAM sites covering 48,175 acres, with 109 miles of affected streams;
- Utah—25,020 acres affected by IAMs, with 83 miles of polluted streams;
- Colorado—20,299 mine openings and 1,298 miles of affected streams;
- California—2,484 IAM sites, 1,685 mine openings, and 578 miles of polluted streams;
- Idaho—27,543 acres affected;
- Oklahoma—26,453 acres affected; and
- New Mexico—25,320 acres and 69 miles of streams affected.

Total remediation costs for these nine states are estimated at more than \$4 billion.

Health effects from the predominate contaminants in mine waste range from mild irritants to proven human carcinogens, such as cadmium and arsenic. The large volume of mine wastes and consequential adverse

environmental and human health effects, indicates an urgency for cleanup of abandoned, inactive, and active mining facilities. The environmental future of the United States depends in part on the ability to deal effectively with mine waste problems of the past and present, and, more importantly, to prevent mine waste problems in the future.

According to a 1985 report to Congress, mining and related activities generate anywhere from 1 to 2 billion tons of waste each year with a current total waste volume of 50 billion tons. Of this total volume, approximately 85% is attributed to copper, iron ore, uranium, and phosphate mining and related activities. Approximately one-half of the waste generated is mining waste and one-third is tailings, with the balance consisting of dump/heap leaching wastes and mine water.

The FY91 Congressional Appropriation allocated \$3.5 million to establish a pilot program in Butte, Montana, for evaluating and testing mine waste treatment technologies. The Mine Waste Technology Program (MWTP) received additional appropriations of \$2.5 million in FY93, \$2.5 million in FY94, \$5 million in FY95, and \$2.5 million for FY96.

The projects undertaken by this Program focus on developing and demonstrating innovative technologies at both the bench-and pilot-scale that treat wastes to reduce their volume, mobility, or toxicity. To convey the results of these demonstrations to the user community, the mining industry, and regulatory agencies, the MWTP includes provisions for extensive technology transfer and educational activities. This report summarizes progress made in FY96 by the MWTP.

PROGRAM OVERVIEW

FISCAL YEAR 1996 PROGRAM

This MWTP annual report covers the period from October 1, 1995, through September 30, 1996. This section of the report explains the organization and operation of the MWTP.

MISSION

The mission of the MWTP is to provide engineering solutions to national environmental issues resulting from the past practices of mining and smelting of metallic ores. In accomplishing this mission, the MWTP develops and conducts a program that emphasizes treatment technology development, testing and evaluation at bench- and pilot-scale, and an education program that emphasizes training and technology transfer. Evaluation of the treatment technologies focuses on reducing the mobility, toxicity, and volume of waste; implementability; short- and long-term effectiveness; protection of human health and the environment; community acceptance; and cost reduction.

The statement of work provided in the Interagency Agreement between the EPA and the U.S. Department of Energy (DOE) identifies six activities to be completed by the MWTP. The following descriptions identify the key features of each and the organization performing the activity.

ACTIVITY I: ISSUES IDENTIFICATION

Montana Tech of the University of Montana (Montana Tech) is documenting mine waste technical issues and innovative treatment technologies. These issues and technologies are then screened and prioritized in volumes related to a specific mine waste problem. Technical issues of primary interest are Mobile Toxic Constituents—Water/Acid Generation, Mobile Toxic Constituents—Air, Cyanide, Nitrate, Arsenic, and Pyrite. Wasteforms reviewed related to these issues include point-

and nonpoint-source acid drainage, abandoned mine acid drainage, stream-side tailings, impounded tailings, priority soils, and heap leach-cyanide/acid tailings.

Montana Tech has developed the means to store and access information regarding mine waste issues and technology by establishing the Science and Technology Information Retrieval System (STIRS).

Many sources of mineral- and mining-related information already exist in the United States and internationally. Created by the MWTP and partially funded by the DOE Resource Recovery Project, STIRS allows immediate and centralized access to many existing data bases and facilitates efficient and comprehensive searches of literature and data for appropriate remediation science, technologies, and processes. The Montana Tech Library in Butte, Montana, houses STIRS. Various data bases, including those developed by EPA, DOE, and the former U.S. Bureau of Mines can be accessed electronically through STIRS. Other resident software and CD-ROM information systems are available to MWTP researchers at the Library. The Montana Tech Library can also provide information on an interlibrary loan basis and can access other resident collections in the United States through an on-line computer search. An information specialist and a part-time research assistant are available in the Montana Tech Library to give assistance in searching appropriate information sources.

ACTIVITY II: GENERIC QUALITY ASSURANCE PROJECT PLAN

Montana Tech has prepared a generic quality assurance project plan that provides specific instructions on how data will be gathered, analyzed, and reported for all activities of the MWTP. Features of both the EPA and DOE quality requirements are incorporated into this plan. Project-specific quality assurance project plans are developed by MSE Technology Applications, Inc. (MSE). MSE provides oversight for all quality assurance activities.

ACTIVITY III: PILOT-SCALE DEMONSTRATIONS

MSE is currently conducting and reporting on three pilot-scale demonstrations of innovative technologies for remediation of mining waste that are operating in the field at remote mine sites. Work has continued on nitrate removal and biocyanide, and work has begun on an additional project—arsenic oxidation. The demonstrations are chosen after a thorough investigation of the technical issue is performed, the specific wasteform to be tested is identified, and a sound engineering and cost determination of the innovative technology is formulated. This activity relies heavily on the list of technologies and wasteforms produced in Activity I.

ACTIVITY IV: BENCH-SCALE EXPERIMENTS

Montana Tech is conducting bench- or small pilot-scale research on several innovative techniques that show promise for cost-effective remediation of mine waste. One major criteria for these projects is the potential for scaling to demonstration pilot plants.

The Berkeley Pit Innovative Technologies Project was initiated during the reporting period to focus on bench-scale testing of remediation technologies to help assist in defining alternative remediation strategies for the EPA's future cleanup objectives for the Berkeley Pit waters. The Berkeley Pit is an inactive, open-pit copper mine that has been filling with acidic water since pump dewatering of adjacent underground mines ceased in 1982.

ACTIVITY V: TECHNOLOGY TRANSFER

MSE is responsible for preparing and distributing reports for the MWTP. These include routine weekly, monthly, quarterly, and annual reports; technical progress reports; and final reports for all MWTP activities. MSE also publicizes information developed under the MWTP in local, regional, and national publications. Other means of information transfer include public meetings, workshops, and symposiums.

ACTIVITY VI: EDUCATIONAL PROGRAMS

Montana Tech has developed a post-graduate degree program with a mine waste emphasis. The program contains elements of geophysical, hydrogeological, environmental, geochemical, mining and mineral processing, extractive metallurgical, and biological engineering.

In FY96, Montana Tech conducted numerous short courses relating to mining waste and provided outreach programs to students in kindergarten through grade 12.

ORGANIZATIONAL STRUCTURE

MANAGEMENT ROLES AND RESPONSIBILITIES

Management of the MWTP is specified in the Interagency Agreement. The roles and responsibilities of each organization represented are described below. The organization chart for the MWTP is presented in Figure 1.

INTERAGENCY AGREEMENT MANAGEMENT COMMITTEE

Under the Interagency Agreement, the EPA and DOE jointly established a management organization comprised of the following principal representatives:

- C The Director designees, Office of Environmental Engineering and Technology Demonstration, Office of Research and Development, EPA; and
- C The Director designees, Office of Science and Technology, Office of Environmental Restoration and Waste Management, DOE.

The Interagency Agreement Management Committee meets periodically for joint project review and approval of the activities under the MWTP.

ENVIRONMENTAL PROTECTION AGENCY

The Director of the Office of Environmental Engineering and Technology Demonstration, Office of Research and Development, is the principal EPA representative on the Interagency Agreement Management Committee and provides program review and approval for the MWTP. Program and technical oversight of the MWTP is provided by EPA's National Risk Management Research Laboratory (NRMRL) in Cincinnati, Ohio. The NRMRL is responsible to the Office of

Research and Development for management oversight of project budget, schedule, and scope.

DEPARTMENT OF ENERGY

The Director of the DOE Office of Science and Technology, Office of Environmental Restoration and Waste Management, is the principal DOE representative on the Interagency Agreement Management Committee and provides program review and approval for the MWTP. MWTP project management is provided by the Federal Energy Technology Center (FETC), which has line responsibility for applying all applicable DOE regulations to the MWTP. The DOE-Western Environmental Technology Office (WETO) is responsible to FETC for management oversight concerning environmental, safety, and health requirements; regulatory actions; and operational conduct of MWTP projects at the WETO in Butte, Montana.

MSE TECHNOLOGY APPLICATIONS, INC.

MSE, under contract with DOE, is the principal performing contractor for the MWTP. The MWTP Program Manager is the point of contact for all mine waste activities. The Program Manager directs the Program through a Senior Project Manager, who is responsible for Program management and coordination, Program status reporting, funds distribution, and communications.

MINE WASTE TECHNOLOGY PROGRAM ORGANIZATIONAL STRUCTURE

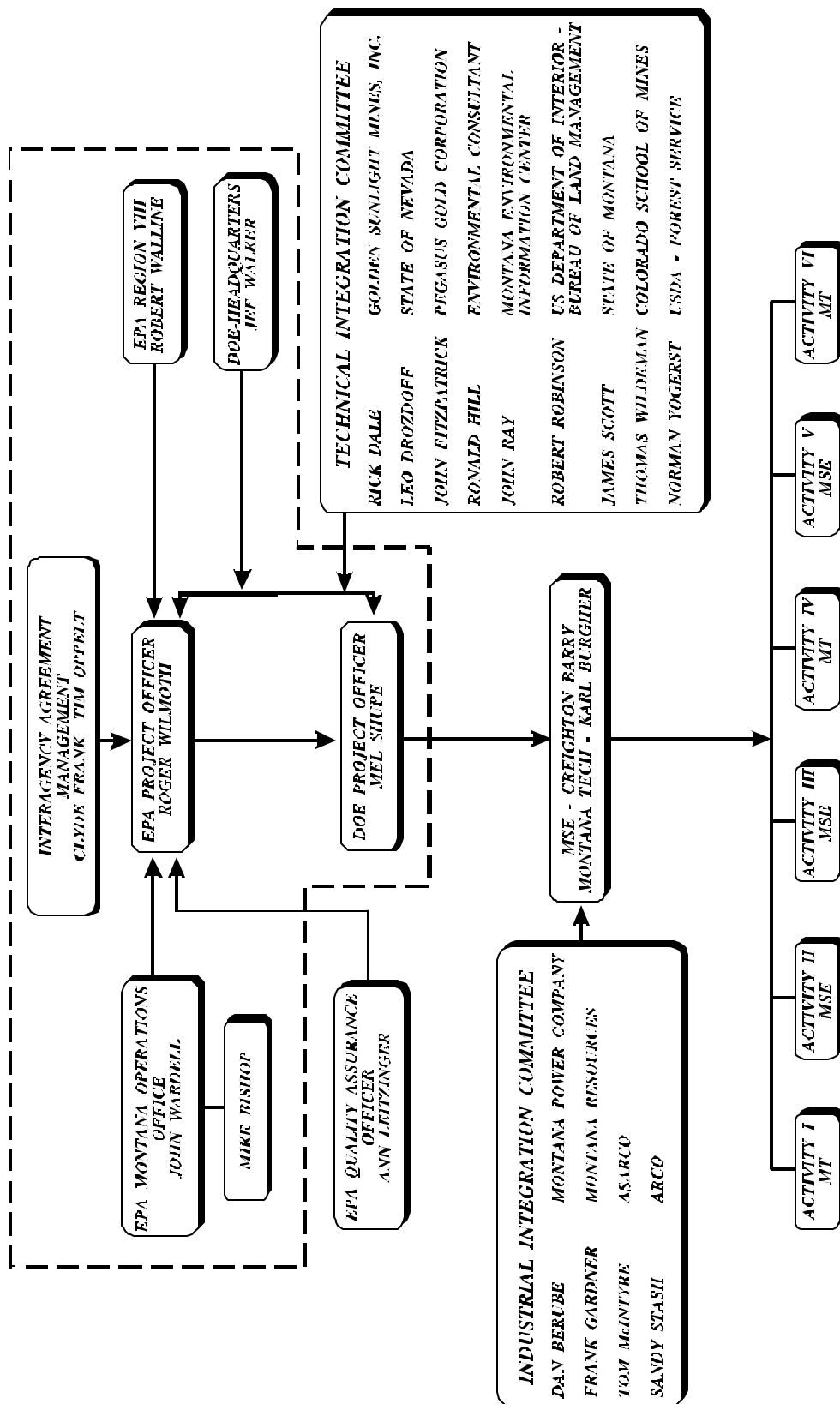


Figure 1. MWTP organizational chart.

An MSE Project Engineer has been assigned to each of the MWTP projects and is responsible to the MWTP Senior Project Manager for overall project direction, control, and coordination. Each Project Engineer is responsible for implementing the project within the approved scope, schedule, and cost. MSE also provides all staff necessary for completing Activities III and V and oversight of Activity II.

MONTANA TECH OF THE UNIVERSITY OF MONTANA

As a subcontractor to MSE, Montana Tech is responsible to the MWTP Program Manager for all work performed under Activities I, II, IV, and VI. The responsibility for overall project direction, control, and coordination of the work to be completed by Montana Tech is assigned to the MWTP Montana Tech Project Manager.

TECHNICAL INTEGRATION COMMITTEE

The Technical Integration Committee is a nine-member committee established to review progress in meeting the goals of the MWTP and to alert the Interagency Agreement Management Committee to pertinent technical concerns. The committee provides information on the needs and requirements of the entire mining waste technology user community and assists with evaluation of technology demonstrations as well as technology transfer. This committee is comprised of representatives from both the public and private sectors.

INDUSTRIAL INTEGRATION COMMITTEE

The Industrial Integration Committee was established by MSE to link industry with the MWTP remediation demonstration projects (Activity III). This committee identifies the remediation needs and requirements of industry, provides evaluations of the technology demonstrations, and assists in the technology transfer required under Activity V.

ACTIVITIES

DESCRIPTIONS, ACCOMPLISHMENTS, AND FUTURE DIRECTION

This section describes Activities I through VI of the MWTP and includes project descriptions, major project accomplishments during FY96, and future project direction.

ACTIVITY I OVERVIEW

This activity focuses on documenting mine waste technical issues and identifying innovative treatment technologies. Issues and technologies are screened and prioritized in volumes related to a specific mine waste problem/market.

Following completion of a volume, appendices are prepared. Each appendix links a candidate technology with a specific site where such a technology might be applied. The technology/site combinations are then screened and ranked.

Another major component of Activity I is the Science and Technology Information Retrieval System (STIRS), discussed in detail below.

Technical Issue Status

The status of the volumes approved for development includes:

- Volume 1, Mobile Toxic Constituents— Water and Acid Generation, complete.
- Volume 2, Mobile Toxic Constituents—Air, complete.
- Volume 3, Cyanide, complete.
- Volume 4, Nitrate, complete.

- Volume 5, Arsenic, complete.
- Volumes 1-5 Summary Report, complete.
- Volume 6, Pyrite, complete.

The status of the appendices for approved projects includes:

- Volume 1, Appendix A (Remote Mine Site), complete.
- Volume 1, Appendix B (Grouting), complete.
- Volume 1, Appendix C (Sulfate-Reducing Bacteria), complete.
- Volume 3, Appendix A (Biocyanide), complete.
- Volume 4, Appendix A (Nitrate), complete.

Science and Technology Information Retrieval System Description

Many sources of mineral- and mining-related information exist in the United States and internationally. STIRS was created by the MWTP to allow immediate and centralized access to these existing data bases. The system provides for efficient and comprehensive literature and data searches for appropriate remediation science, technologies, and processes. STIRS is housed at the Montana Tech Library in Butte and is under the direction of the Library Director.

The basic components of STIRS are:

- access to existing electronic data bases;
- access to publications; and
- preparation of specialized data bases to access MWTP information.

These specialized data bases are internally created STIRS data bases I and II. STIRS I contains MWTP research reports and local public documents, and STIRS II includes reviews of technologies. Many data bases,

including those developed by the EPA, DOE, and the former U.S. Bureau of Mines, can be accessed through STIRS. This provides an efficient method of single-point access without duplication.

Other resident software and CD-ROM information systems are available to MWTP researchers. The Montana Tech Library also provides interlibrary loans and can access other resident collections in the United States through on-line computer searches.

Science and Technology Information Retrieval System Status

The following data bases are available:

- Classification and Search Support Information System (CASSIS). The Montana Tech Library is an official U.S. Patent and Trademark depository. Copies of all patents since 1981 are on microfilm; many older patents are also available.
- The Vendor Information System for Innovative Treatment Technologies (VISITT) was created by EPA to help select technologies for the remediation of contaminated sites.
- Remedial Options (ReOpt) enables quick identification of applicable, proven remediation technologies for a waste site.
- Cleanup Information Bulletin Board (CLU-IN) provides access to various data bases dealing with cleanup technologies.
- Alternative Treatment Technology Information Center (ATTIC) provides on-line information about treatment systems for remediation of contaminated sites.
- Records of Decision (RODs) provide full-text official ROD documents signed and issued by the EPA.
- State Administrative Records consist of five bibliographic indexes for the Upper Clark Fork Basin.

- IMAGE contains information about nonferrous metals and industrial minerals.
- WILSONDISC gives access to applied science/technology, general science, and agricultural/biological citations.
- MARCIVE includes documents from the U.S. Government Printing Office.
- Environmental Library provides full-text federal and Montana State environmental laws, regulations, and related documents.
- GeoRef indexes geoscience publications.
- Water Resources Abstracts offers global coverage of water chemistry since 1967.

The following relevant on-line bibliographic data bases are available:

- QuickLaw is a Canadian data base that provides access to MINTEC (mining technology) and MINPROC (mineral processing technology) data bases.
- DIALOG is an on-line data base that combines bibliographic listings from data bases around the world.

From a central location, STIRS allows users to access a vast amount of information relevant to mine waste remediation technologies. By using this up-to-date retrieval system along with other information, screening and selecting a cleanup method for inactive or abandoned mine sites can now be fast, easy, and comprehensive.

Future Activities

STIRS will continue to build the internal data bases, acquire additional national and international external data bases, and provide access to relevant Internet sites, making them available to program participants and the public.

As technology demonstration and research projects produce results, they will be added to the STIRS internal data base I.

Technology summaries will continue to be entered into STIRS internal data base II as they are received.

The external and internal data base capabilities will be summarized and distributed to researchers and the public to create an awareness of the STIRS system.

ACTIVITY II OVERVIEW

The objective of this activity is to provide support to individual MWTP projects by ensuring all data generated is legally and technically defensible and that it supports the achievement of individual project objectives. The primary means of carrying out this activity is the quality assurance project plan, which is written for each project. This plan specifies the quality requirements the data must meet, clearly states the project objectives, describes all sampling and measurement activities, and contains standard operating procedures, when applicable. Other functions of this activity include reviewing technical systems, validating data, implementing corrective action, and reporting to project management.

Activity II, Preparing a Generic Quality Assurance Project Plan, was completed during FY92 and includes continuing quality assurance activities; therefore, no detailed section for Activity II is included in this report. Specific quality assurance project plans were prepared for individual projects and are described in the appropriate sections.

ACTIVITY III OVERVIEW

The objective of this activity is to demonstrate innovative and practical remedial technologies at selected waste sites, a key step in proving value for widespread use and commercialization. Technologies and sites are selected primarily from the prioritized lists generated in the Volumes from Activity I, or they may be a scaleup from bench-scale experiments conducted under Activity IV.

ACTIVITY III, PROJECT 1: REMOTE MINE SITE DEMONSTRATION

Project Overview

Acidic metal-laden water draining from remote, abandoned mines has been identified by the EPA as a significant environmental hazard to surface water in the Western United States. In Montana alone, more than 3,000 such sites have been identified, and wastes from these mines have damaged over 1,100 miles of surface water in the State.

The EPA asked MSE to develop a treatment facility at one of these sites to treat acidic metal-laden water. Due to the remote nature of these locations, this facility must operate for extended periods of time on water power alone, without operator assistance.

An example of a remote mine site with a point-source aqueous discharge is the Crystal Mine. Located 7 miles north of Basin, Montana, the Crystal Mine was an ideal site for this demonstration. In addition, the site had been identified by the Montana State Water Quality Bureau as a significant contributor of both acid and metal pollution to Uncle Sam Creek, Cataract Creek, and the Boulder River. This project demonstrated a method for alleviating nation-wide environmental problems associated with remote mine sites.

Technology Description

The Crystal Mine demonstration treated a flow of water ranging from 10 to 25 gallons per minute, approximately half of the total mine discharge. The process consisted of the following six unit operations arranged as shown in Figure 2.

- Initial Oxidation—atmospheric oxygen partially oxidizes ferrous iron to the ferric form.
- Alkaline Addition—reagents form metal hydroxide solids.
- Secondary Oxidation—atmospheric oxygen oxidizes additional ferrous iron to the ferric form.
- Initial Solid/Liquid Separation—settling ponds trap precipitated solids.
- pH Adjustment—atmospheric carbon dioxide lowers the pH.

- Secondary Solid/Liquid Separation—settling pond retains additional precipitated solids.

Status

The Remote Mine Site Demonstration Project at the Crystal Mine was to be conducted in the field for a minimum of 1 year under all weather conditions. Construction of buildings, ponds, and associated mine site infrastructure began in late May 1994 and was completed in early August 1994. Acid mine drainage from the lower portal of the Crystal Mine began passing through the system on a full-time basis in early September 1994. Initial analytical data from the project showed a greater than 90% removal of toxic metals from the mine drainage. The system was operated and data was collected for 2 years. The project is being closed out, and the final report is being prepared.

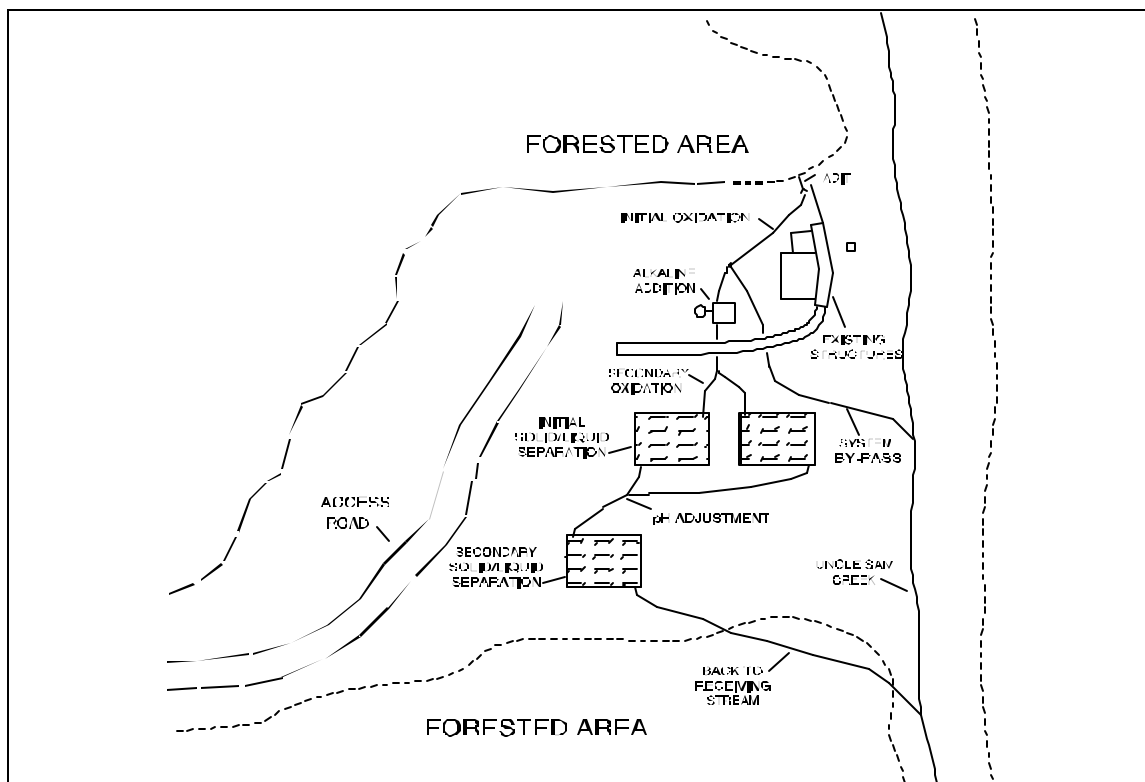


Figure 2. Crystal Mine water treatment system plan view.

ACTIVITY III, PROJECT 2: CLAY-BASED GROUTING DEMONSTRATION

Project Overview

Surface and groundwater inflow into underground mine workings becomes a significant environmental problem when water contacts sulfide ores, forming acid drainage. Clay-based grouting, the technology selected for this demonstration, has the ability to reduce or eliminate water inflow into mine workings by establishing an impervious clay curtain in the formation.

Technology Description

Groundwater flow is the movement of water through fissures and cracks or intergranular spaces in the earth. With proper application, grout can inhibit or eliminate this flow.

Grouting is accomplished by injecting fine-grained slurries or solutions into underground pathways where they form a groundwater barrier. The Ukrainian clay-based grouting technology was selected for testing and evaluation because it offered a potentially long-term solution to acid mine drainage problems.

The demonstration consisted of three phases: 1) extensive geologic studies, 2) grout formulation, and 3) grout placement.

Phase One consisted of site characterization studies, including geophysical, geochemical, mineralogical, and hydrogeologic information directly related to the mine and its past operational procedures.

Phase Two encompassed the grout formulation. Clay-based grouts are viscoplastic systems primarily comprised of structure-forming cement and clay-mineral mortar. When compared to cement-based

grouts, clay-based grouts offer the following advantages: better rheological characteristics, greater retention of plasticity through the stabilization period, and less deterioration during small rock movement.

Phase Three consisted of grout placement. Grout was pumped into boreholes using packers to ensure grout was placed at proper intervals.

Status

The project was finalized at the Mike Horse Mine near Lincoln, Montana. This site was selected because of its geologic characteristics. A major factor in the selection was an identified point-source inflow from Mike Horse Creek into the mine causing acid drainage that could potentially be controlled using a grouting technology.

Phase One was completed in August 1994. Phase Two was performed in the Ukraine by Spetstamponazhgeologia Enterprises (STG) and was completed in May 1994. Hayward Baker, Inc., was awarded the subcontract to inject the clay-based grout, and they arrived at the Mike Horse Mine site during the first week of September 1994. Grout injection began September 20, 1994, and was completed November 1, 1994.

Approximately 1,600 cubic yards of grout were injected during this initial phase. A second phase of grout injection was planned for the summer of 1995; however, high water dammed up within the mine caused extensive damage to the mine and to the monitoring stations used for the demonstration. As a result, Phase Two was discontinued.

A draft interim report was completed during July 1996, and a final report is scheduled to be completed in FY97.

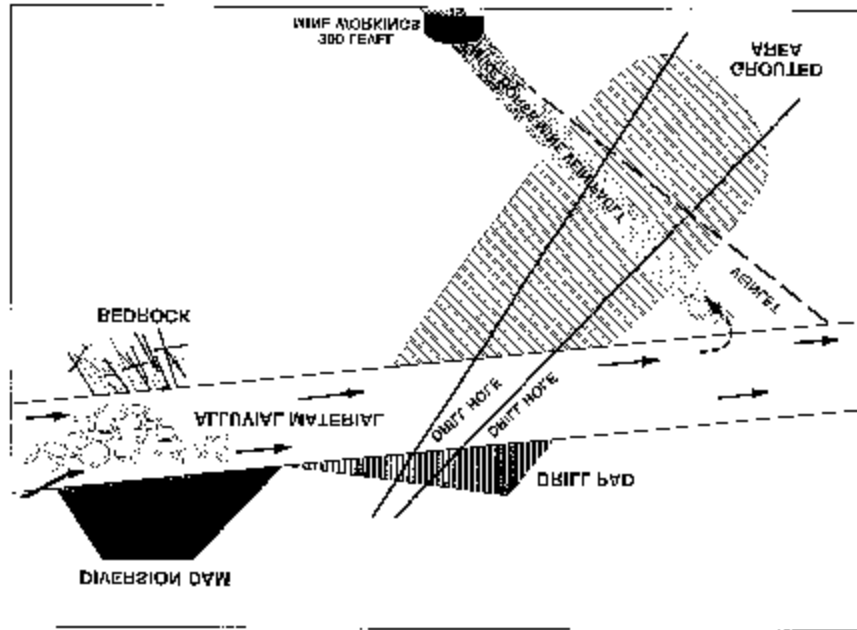


Figure 3. Cross-section of grouting demonstration project.



Figure 4. Grouting activities at the Mike Horse Mine.



Figure 5. Grouting activities at the Mike Horse Mine.

ACTIVITY III, PROJECT 3: SULFATE-REDUCING BACTERIA DEMONSTRATION

Project Overview

Acid generation typically accompanies sulfide-related mining activities and is a widespread problem. Acid is produced chemically, through pyritic mineral oxidation, and biologically, through bacterial metabolism. This project focuses on a source-control technology that has the potential to significantly retard or prevent acid generation at affected mining sites. Biological sulfate reduction is being demonstrated at an abandoned hard-rock mine site where acid production is occurring with associated metal mobility.

Technology Description

For aqueous waste, this biological process is generally limited to the reduction of dissolved sulfate to hydrogen sulfide and the concomitant oxidation of organic nutrients to bicarbonate. The particular group of bacteria chosen for this demonstration, sulfate-reducing bacteria (SRB), require a reducing environment and cannot tolerate aerobic conditions for extended periods. These bacteria require a simple organic nutrient.

This technology has the potential to reduce the contamination of aqueous waste in three ways. First, dissolved sulfate is reduced to hydrogen sulfide through metabolic action by the SRB. Next, the hydrogen sulfide reacts with dissolved metals forming insoluble metal sulfides. Finally, the bacterial metabolism of the organic substrate produces bicarbonate,

increasing the pH of the solution and limiting further metal dissolution.

At the acid-generating mine site chosen for the technology demonstration, the Lilly/Orphan Boy Mine near Elliston, Montana, the aqueous waste contained in the shaft is being treated by using the mine as an in situ reactor. An organic nutrient comprised mainly of cow manure was added to promote growth of the organisms. This technology will also act as a source control by slowing or reversing acid production. Biological sulfate reduction is an anaerobic process that will reduce the quantity of dissolved oxygen in the mine water and increase the pH, thereby slowing or stopping acid production.

The shaft of the Lilly/Orphan Boy Mine was developed to a depth of 250 feet and is flooded to the 74-foot level. Acid mine water historically discharged from the portal associated with this level.

Pilot-scale work at the WETO in Butte was performed in FY94. The objective of these tests was to determine how well bacterial sulfate reduction lowers the concentration of metals in mine water at the shaft temperature (8 °C) and pH (3.0).

Status

During FY96, the field demonstration was again monitored on a regular basis. Figure 6 presents a cross-section of the mine and technology installation. Discharge reports were submitted to the Montana Department of Environmental Quality on a monthly basis and to the EPA, Region VIII, on a quarterly basis.

The report of the pilot-scale demonstration was completed in FY95 and submitted to EPA's NRMRL. Final publication of the document was postponed until further adsorption studies could be completed per the request of NRMRL. The adsorption studies were initiated in FY96 and are being conducted by Montana State University-Bozeman.

The project underwent a technical review at NRMRL during July 1996.

A technical paper on the project was presented at the Minerals Bioprocessing and Biorecovery/Bioremediation in Mining Conference that was held in Big Sky, Montana, in August 1996.

During the second year of monitoring, the data generally demonstrated a decrease in metals concentrations (see Figure 7). An increase in metals was observed during spring runoff; however, the levels decreased when flow rates returned to normal. Monitoring of the field demonstration will continue for an additional year.

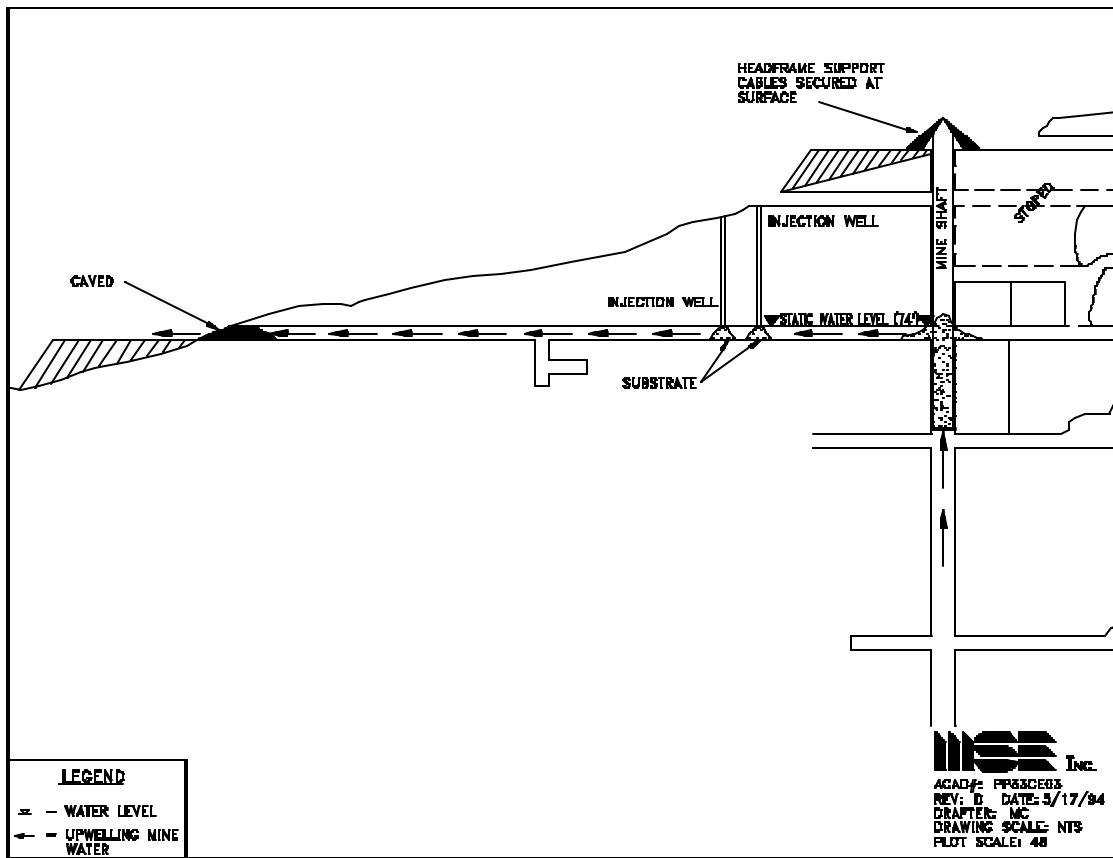


Figure 6. Cross-section of the Lilly/Orphan Boy Mine and the technology installation.

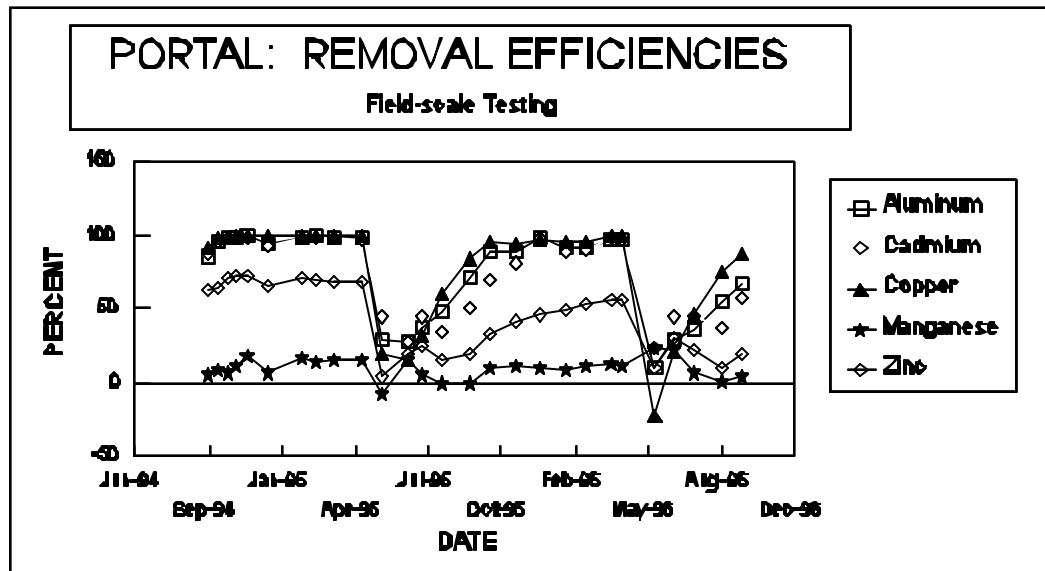


Figure 7. Metal removal efficiency at the Lilly/Orphan Boy Mine.

ACTIVITY III, PROJECT 4: NITRATE REMOVAL DEMONSTRATION

Project Overview

The presence of nitrates in water can have detrimental effects on human health and the environment. As a result, regulatory agencies have limited the allowable concentration of nitrates in effluent water.

Nitrates may be present in mine discharge water as a result of the following mining activities:

- residuals from ammonium nitrate and fuel oil (ANFO) used in blasting;
- cyanide breakdown from leaching;
- leaching of ANFO contamination from waste rock or from rock with naturally occurring nitrate; and
- residuals from fertilizer used in reclamation.

To comply with Federal and state water quality standards, mining companies have typically used ion exchange or reverse osmosis to remove nitrates from discharge water. Both, however, are expensive and generate a concentrated wastestream requiring disposal.

Technology Description

MWTP personnel undertook an extensive search to evaluate innovative technologies to resolve the nitrate problem. Of the 20 technologies screened, the following 3 showed the most promise in making nitrate removal more cost effective and environmentally responsible:

- ion exchange with nitrate-selective resin;
- biological denitrification; and
- electrochemical ion exchange (EIX).

MWTP personnel believe the best solution to the nitrate problem is some combination of the three technologies that balances capital costs with operating costs, reliability, and minimization of wastestreams requiring disposal. Each combination has advantages and disadvantages that will be addressed during the project.

A test process train was developed that is flexible and optimizes equipment capital while acquiring value-added test data. The demonstration included the following innovative technologies as arranged in Figure 8:

- ion exchange combined with biological denitrification for destruction of the concentrated brine;
- ion exchange combined with EIX for destruction of the concentrated brine;
- biological denitrification as a stand-alone process; and
- EIX as a stand-alone process.

Status

The Nitrate Removal Demonstration Project was conducted at the TVX Mineral Hill Mine near Gardiner, Montana, where a building to house the equipment was constructed. Figure 8 shows the equipment layout for the project. Conventional ion exchange was used to remove nitrates from the mine water and produce a concentrated brine for additional testing. Biological denitrification units and an EIX unit were used to process both mine water and concentrated nitrate brine.

The goals of the project were to remove nitrate to less than 10 milligrams per liter (mg/L) of nitrate-nitrogen ($\text{NO}_3\text{-N}$) in the effluent and to minimize the amount of waste produced. Of all the technology combinations tested, biological denitrification of concentrated nitrate brine was the most successful at meeting these goals.

Due to funding and equipment delivery delays, most of the testing was conducted during the early part of 1996 when extremely cold weather caused the mine water inlet pipe to freeze periodically. The freezing problem was finally alleviated; however, testing was delayed by the frequent shutdowns. With warmer weather, large quantities of silt appeared in the mine portal discharge. This was not anticipated and caused numerous delays while filtering mechanisms were installed.

The nitrate ion exchange (NIX) unit was produced by Selentec, Inc. Ion exchange is a conventional, well-understood technology. As expected, the NIX unit worked well and removed nitrate from the mine water very effectively. Input levels of 20 to 40 mg/L NO_3^- -N were typically reduced to less than 1 mg/L. The unit also produced a concentrated brine with the predicted levels of nitrate and chloride. Frequent equipment shutdowns and muddy mine water did not affect the operation of the NIX unit.

Biological denitrification was performed on both mine water and concentrated brine. As shown in Figure 9, this process worked well to eliminate nitrate in brine. Except for two process upsets (one caused by a large concentration increase), nitrate was removed to levels less than 10 mg/L NO_3^- -N. This removal rate met the project goals and was typically greater than 99%.

Biological denitrification of the raw mine water was less successful. A removal rate of approximately 50% was typically achieved. This data was taken from an

operating denitrification reactor at the mine. Past data had shown that this reactor was very effective at nitrate removal. Apparently the frequent shutdowns and startups had a much more detrimental effect on these reactors.

Electrochemical ion exchange was unsuccessful at removing much nitrate from the concentrated brine because of the presence of high concentrations of a competing anion—chloride. Even though the ion exchange resin had a high affinity for nitrate ions, the 30:1 ratio of chloride ions to nitrate caused a continuous regeneration of the resin back to the chloride form and very little collection of nitrate.

Electrochemical ion exchange was able to remove nitrate from the raw mine water more effectively than from the brine. Nitrate was removed at first; however, fouling of the resin by dirty water occurred quickly, and the process was rendered ineffective after one batch. Filters were installed to alleviate the problem, but the size and nature of the particles made filtration difficult. Midway through the test sequence, the dirty resin was removed and replaced with clean resin. This worked for a while, but the resin was quickly fouled and rendered ineffective.

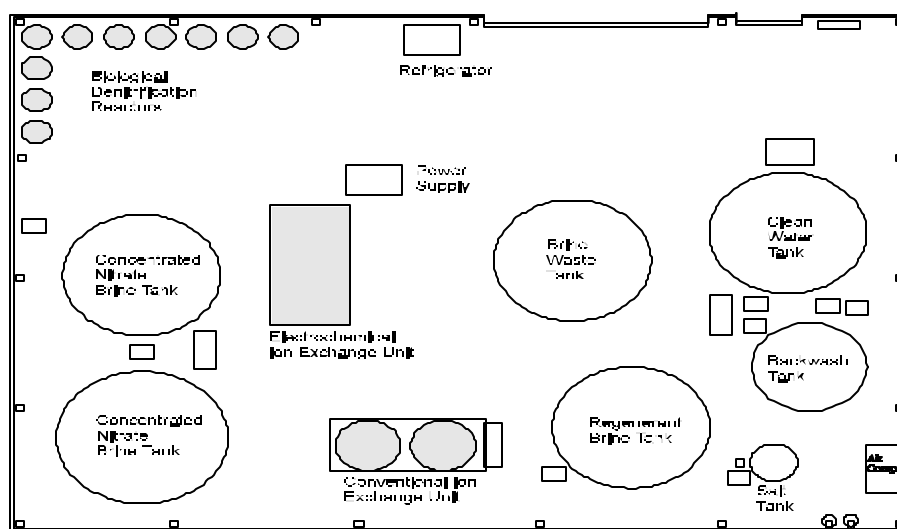


Figure 8. Nitrate Removal Demonstration Project equipment layout.

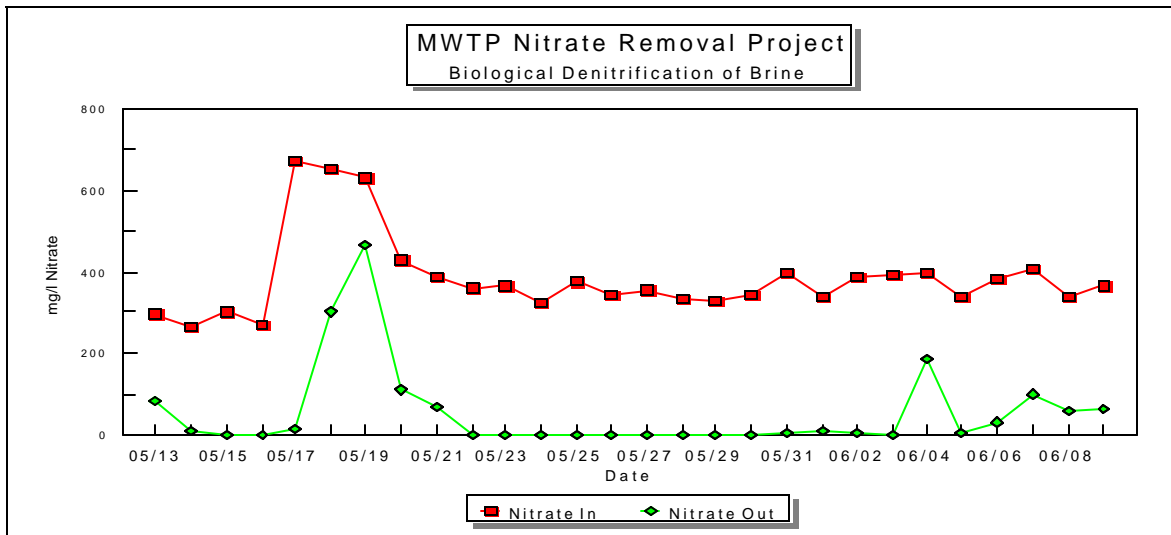


Figure 9. Data showing nitrate removal in brine (1996).

ACTIVITY III, PROJECT 5: BIOCYANIDE DEMONSTRATION

Project Overview

The primary use of cyanide in the mining industry is to extract precious metals from ores, and the use of cyanide has expanded in recent years due to increased recovery of gold using heap leach technologies. Cyanide can be an acute poison and can form strong complexes with several metals, resulting in increased mobility of those metals. As such, cyanide in mine wastewater can contribute to environmental problems.

These potential problems have led to the development of several methods to destroy cyanide and cyanide complexes in mining wastewater. Most of these processes use chemicals to oxidize the cyanide and produce nontoxic levels of carbon dioxide and nitrogen compounds. These are relatively expensive to operate.

Technology Description

Biological destruction of cyanide compounds is a natural process that occurs in soils and dilute solutions. To take advantage of this natural destruction, a strain of bacteria was isolated by researchers at Pintail Systems, Inc. This bacteria has been tested on cyanide-

contaminated mine waters and has shown degradation rates of over 50% in 15 minutes.

The main goal of this project is to use a strain of bacteria to destroy cyanide associated with precious metal mining operations. Another project goal is to develop a reactor design that will best use the cyanide-degrading effects of the bacteria to destroy cyanide from mining wastewater.

The field demonstration portion of the project is located at the Echo Bay McCoy/Cove Mine, southwest of Battle Mountain, Nevada. The mining rate at the mine exceeds 160,000 tons of ore per day. Milling of high-grade and sulfide ores occurs simultaneously with the cyanide solution heap leaching of lower grade ores. These cyanide solutions contain 500 to 600 mg/L of weak acid dissociable (WAD) cyanide with other contaminants, such as arsenic, copper, mercury, selenium, silver, zinc, and nitrate.

Status

In FY96, a field-scale unit was constructed at the McCoy/Cove Mine to degrade cyanide in an existing process stream. The unit was designed to reduce the WAD cyanide concentration from 500 mg/L to less than 0.2 mg/L at flow rates of approximately 1 gallon

per minute.

A bioaugmentation phase was initiated to isolate organisms and select the ones that degrade cyanide most effectively. To initiate the project, Pintail Systems, Inc., collected water samples from the mine site to isolate indigenous organisms capable of effectively degrading cyanide and performed bioaugmentation studies at their Colorado laboratory. During the bioaugmentation phase, the bacteria were subjected to increasing concentrations of cyanide to select for the most capable organisms.

The bacteria selected during the bioaugmentation process were then placed on fixed growth media in bench-scale reactors. Next, actual cyanide mine water was processed through the reactors to study the kinetics of cyanide degradation. The results from these

tests were then used to design the pilot-scale reactors to be used at the mine. The final process train, which includes both aerobic and anaerobic cyanide-degrading organisms, is shown in Figure 10. The process train consists of tanks where the aerobic and anaerobic bacteria are grown in large quantities. The bacteria are then pumped to the reactors for reinoculation. The cyanide solution enters the aerobic reactor first where aerobic organisms degrade a large portion of the cyanide. The solution then moves through a series of anaerobic units for further degradation. Finally, an aerobic polishing step removes the last traces. Since cyanide is known to degrade by mechanisms other than biological, a series of control reactors was installed to run concurrently with the biological reactors.

Actual testing had not yet begun at the end of FY96. Testing will occur during FY97.

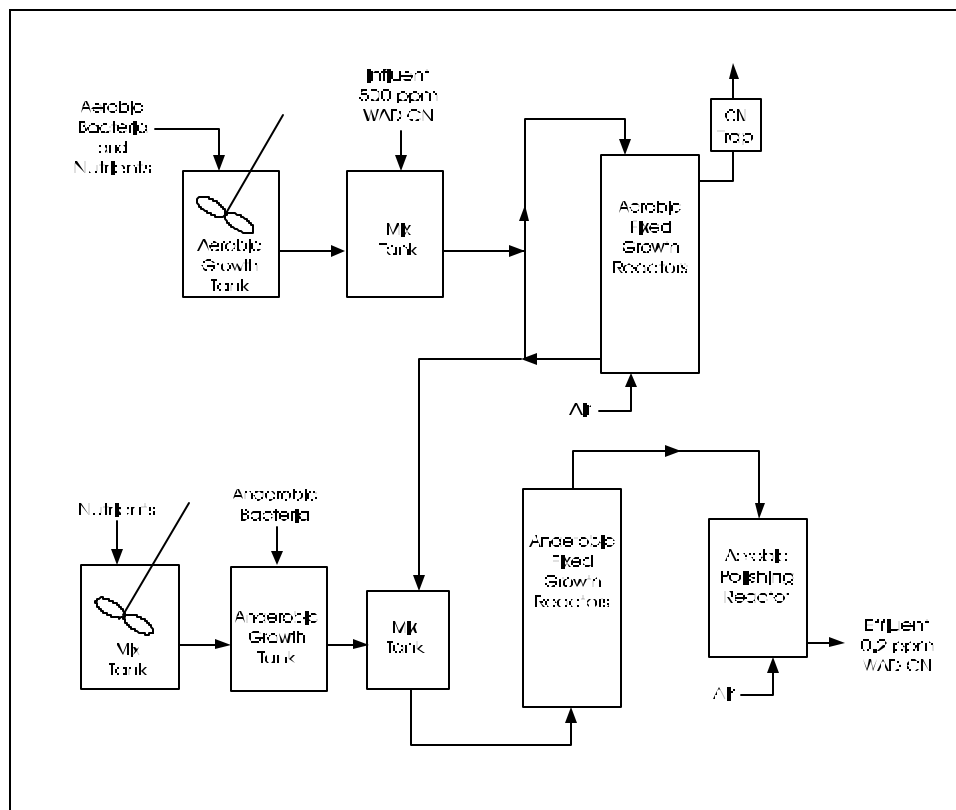


Figure 10. Biocyanide Demonstration Project.

ACTIVITY III, PROJECT 6: POLLUTANT MAGNET

Project Overview

This project was forwarded to the MWTP by personnel from EPA's NRMRL. The concept of the pollutant magnet is to develop, produce, and test particles that have specific magnetic properties and have the ability to remove specific pollutants from a wastestream.

Status

A series of initial meetings on the project were held and involved personnel from EPA-NRMRL, MSE, DOE, the former U.S. Bureau of Mines, and researchers from the Universities of Arizona and Missouri-Rolla. Subsequent to these meetings, the pollutant magnet project was dropped from the MWTP due to its similarity with competing technologies that were more developed and had a nonmining specific use.

ACTIVITY III, PROJECT 7: ARSENIC OXIDATION

Project Overview

The Arsenic Oxidation Project was proposed to demonstrate and evaluate arsenic oxidation and removal technologies. The technology being demonstrated during this project was developed jointly by the Cooperative Research Center for Waste Management and Pollution Control Limited (CRC-WMPC) and the Australian Nuclear Science & Technology Organization (ANSTO) from Lucas Heights Research Laboratories in Lucas Heights, New South Wales, Australia.

Arsenic contamination in water is often a by-product of mining and the extraction of metals such as copper, gold, lead, zinc, silver, and nickel. This contamination will continue to grow as high-grade ores with low arsenic content are being depleted and the processing of sulphide ores with high arsenic content becomes increasingly common. In most cases, it is not economical to recover the arsenic contained in process streams because there is little demand worldwide for arsenic. Arsenic can be present in leachates from piles of coal fly ash, in contaminated groundwaters, in geothermal waters, and in acid drainage from pyritic heaps that result from the past practices of mining of metallic ores.

Trivalent arsenic, arsenic(III), or arsenite compounds have been reported to be more toxic than the corresponding pentavalent arsenic, arsenic(V) or arsenate forms, and much more difficult to remove from solution. Consequently, there is a need to convert arsenic(III) to arsenic(V) to achieve effective arsenic removal from solution.

Technology Description

The small-scale pilot project demonstrated a two-step process for removing arsenic from contaminated mine water. The first step and primary objective of this project was to evaluate the effectiveness of a photochemical oxidation process to convert dissolved arsenic(III) to arsenic(V) using dissolved oxygen as the oxidant. The technology provides a method for the oxidation of arsenic(III) in solution by supplying an oxidant, such as air or oxygen, and a nontoxic photo-absorber, which is capable of absorbing photons and increasing the rate of arsenic(III) oxidation to the solution. The photo-absorber used is economical and readily available. Ultraviolet

oxidation using high-pressure mercury lamps and solar energy was tested. The second step of this project resulted in the removal of arsenic(V) from the solution by using an accepted EPA method, adsorption using ferric iron (see Figure 11).

Status

The field demonstration was completed, and MSE is working with ANSTO to complete the final report. The photochemical oxidation process was very effective at

oxidizing arsenite to arsenate at optimum conditions in the batch mode for both the solar tests and the photoreactor tests; however, design problems with the photoreactor unit in the continuous mode would not allow ANSTO to achieve their claim of 90% oxidation of arsenite in solution. Channeling of the process waters in the photoreactor unit was the reason for poor oxidation of arsenite, and steps to correct the problem during the field demonstration were unsuccessful. Modifications to the baffle system are necessary to prevent further channeling.

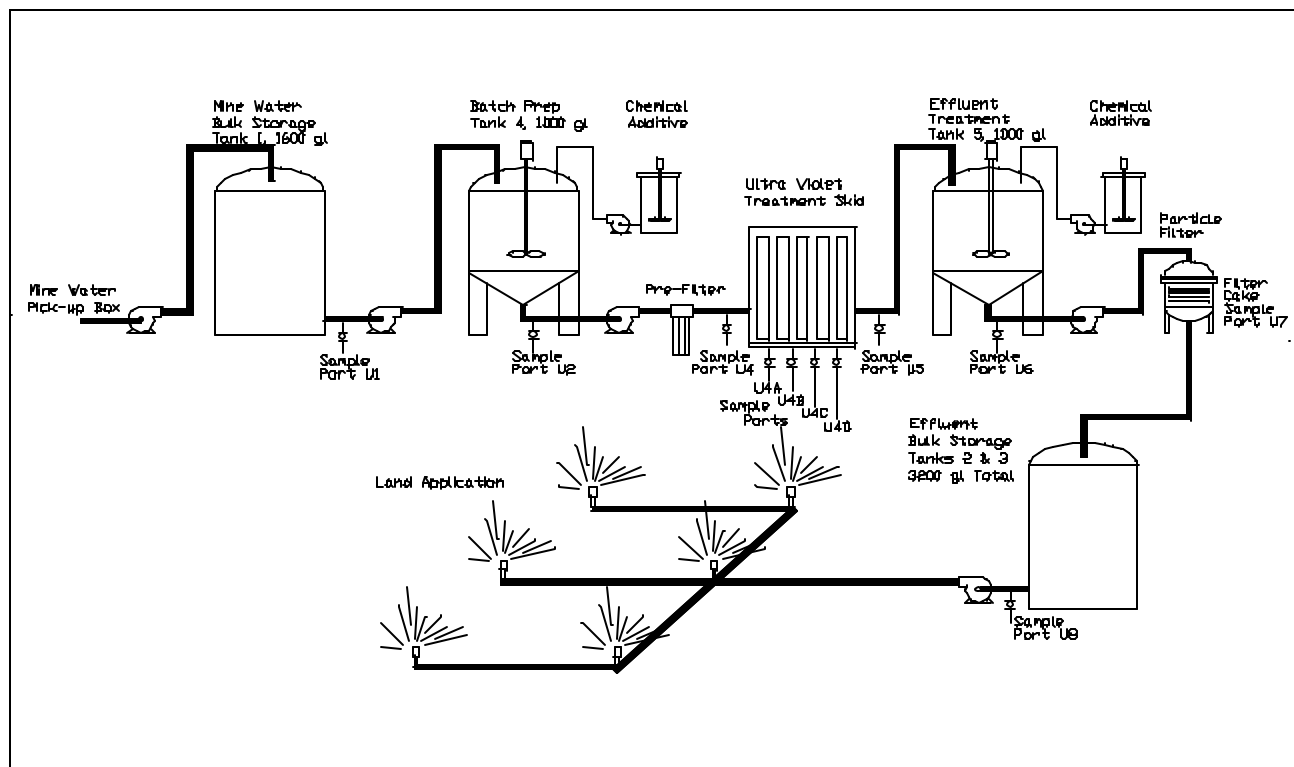


Figure 11. Photoreactor UV arsenic oxidation and removal, batch or continuous flow methods.

ACTIVITY IV OVERVIEW

The objective of this activity is to develop,

qualify, and screen techniques that show promise for cost-effective remediation of mine waste. The most promising and innovative techniques will undergo bench- or pilot-scale evaluations and applicability studies to provide an important first step to full-scale field demonstrations. Each experiment is assigned as an approved project with specific goals, budget, schedule, and principal team members.

ACTIVITY IV, PROJECT 1: BERKELEY PIT WATER TREATMENT

Project Overview

Bench-scale research on treatment of water from the Berkeley Pit is being performed at Montana Tech, in Butte, Montana.

The Berkeley Pit is an abandoned open-pit copper mine in Butte that has been filling with acidic water since pump dewatering of adjacent underground mines ceased in 1982. Flow into the Berkeley Pit has varied from approximately 7.5 million gallons per day (mgd) initially to a current rate of approximately 2.5 mgd.

The water in the Berkeley Pit was chosen for this project due to its accessibility, abundance, and the chemical similarities between it and other acidic mine waters. Studies have been conducted since 1986 on the Berkeley Pit water, and a large amount of analytical data has been previously developed, providing a foundation for this project.

Technology Description

This project addresses treatability of the acid mine water that is accumulating in the Berkeley Pit. Appropriate treatment techniques were identified and developed. The overall goal was to evaluate technologies that produce clean water, allow for safe waste disposal, and recover selected metals for resale. Technologies were evaluated by considering their effectiveness, technical

feasibility, and potential for technology transfer to similar sites.

Experimental testing consists of four major phases:

Physical oxidation, neutralization, and metal removal—this phase consists of using alkaline reagents such as lime, limestone, or soda ash to neutralize the water and cause metals to precipitate as hydroxides. During neutralization, the water is aerated to oxidize iron (II) to iron (III), thereby enhancing sludge settling characteristics and promoting adsorption reactions. Metals removal efficiency and reaction kinetics were studied.

Metals separation and recovery—this phase is a two-stage hydroxide precipitation process. Sulfide and hydroxide precipitation were combined for more complete removal of metals. In other tests, metal sulfides were precipitated first to recover metal value, and scrap iron was used to cement copper before neutralization.

Use of milling waste—this phase consists of adding tailings slurry (primarily silicates, clay, lime, and limestone) directly to the Berkeley Pit water. This partially neutralized the water and removed some of the heavy metals. This in situ neutralization could potentially reduce reagent consumption and sludge formation for subsequent processing.

Diversion and treatment of various inflow water sources—this phase consists of investigating numerous water sources to determine the feasibility of diverting inflow water for treatment. Of the water that flows into the Berkeley Pit, one-third is surface water from the Horseshoe Bend area, and two-thirds is underground water that has penetrated through the mines and surrounding rocks.

Status

All work for this project was completed. The final report has been reviewed and is ready for publication.

ACTIVITY IV, PROJECT 2: SLUDGE STABILIZATION

Project Overview

The Sludge Stabilization Project for mine waste is a bench-scale research project being conducted at Montana Tech.

The purpose of this research project was to study the properties and stability of sludges generated by remediation of acid mine waters. Results of the study were used to determine the best methods for sludge handling and disposal. One source of acid mine water being studied was from the Crystal Mine, which is located approximately 7 miles north of Basin, Montana. The other source was the water from the Berkeley Pit in Butte, Montana. Besides being acidic, these waters contain toxic concentrations of iron, manganese, copper, zinc, arsenic, and sulfate, which is typical of many hard rock mining operations throughout the Western United States.

Past research on remediating acid mine water has focused primarily on water treatment techniques, and little emphasis has been placed on the stability of the sludge that is generated. To address this issue, faculty at Montana Tech, with expertise in chemistry, geochemistry, metallurgy, and environmental engineering, have formed a research team to study the properties and stability of this sludge.

Technology Description

The three types of sludge studied were: base-initiated sludge, inorganic sulfide-initiated sludge, and sulfate-reducing bacteria-initiated sludge. Appropriate solid-liquid separation techniques were used to isolate the solid phases for chemical characterization and stability tests.

Chemical characterization studies included quantifying the various element-solid associations, i.e., adsorbed, surface-precipitated, and coprecipitated contaminants. These studies then identified and quantified the divalent and trivalent forms of iron and the

trivalent, pentavalent, and methylated forms of arsenic. Once analytical techniques were verified for each of the sludges, they were applied to as-generated sludge and aged sludge.

Based on the chemical properties of these sludges, various storage environments were proposed and evaluated. The sludge stability research included standard regulatory tests and specifically designed tests, e.g., biostability tests, based on the selected specific disposal options, including storage in the natural environment. The results of these tests were translated into stability-enhancement studies, including the effect of aging the sludge in a temporary storage environment and treating the sludge with chemical additives before final storage.

The results of this sludge characterization and stability study identified characterization techniques and stability procedures that have application to sludges generated through other water-treatment procedures.

Status

All work for this project was completed. The final report was written and is being reviewed.

ACTIVITY IV, PROJECT 3: PHOTOASSISTED ELECTRON TRANSFER REACTIONS RESEARCH

Project Overview

Current research efforts under the MWTP for the remediation of mine wastewaters have focused primarily on removing toxic heavy metal cations from solution. However, little attention has been given to toxic anions that can be associated with the heavy metal cations. Conventional treatment technologies generally require chemical process streams that generate sludge by-products. Consequently, researchers at Montana Tech are attempting to identify and enhance naturally occurring processes that would help remediate toxic anions while minimizing treatment by-products. In this regard, the use of dissolved and solid photocatalysts is being investigated for the removal of cyanide and nitrate anions from mine wastewaters.

Technology Description

On absorption of electromagnetic radiation (predominantly UV or visible light), photocatalysts enter an excited state where electrons are promoted from a valence band into a conduction band (see Figure 12). Electrons in conduction bands can then be donated to species, causing that species to undergo reduction. Simultaneously, the absence of electrons in the valence band can cause other species to donate electrons

to the valence band and thereby undergo oxidation. These electron-transfer reactions can cause the species to decompose. However, decomposition can only occur if the electrochemistry of the system is well defined, e.g., oxidation-reduction potential, pH, concentration, and temperature, and if the proper intensity and frequency of electromagnetic radiation is available. This radiation may be natural sunlight but inevitably must be artificial to accommodate seasonal, daily, and hourly changes due to winter, nightfall, and cloudiness.

Solid photocatalysis is a proven technology while dissolved photocatalysis is relatively new. With solid photocatalysis, reactions only occur if the species are adsorbed at the surface of the solid photocatalyst. The overall rate of the photocatalytic reactions are thus dependent on the concentration of the species, the rate of adsorption of the species, the available surface area of the photocatalyst, and the rate of desorption of the decomposition products. With dissolved photocatalysts, reactions occur in bulk solution and are only dependent on concentration. Consequently, reaction kinetics with dissolved photocatalysts can be at least three orders of magnitude faster than with solid photocatalysts.

Status

All work for this project was completed. The final report was written and is being reviewed.

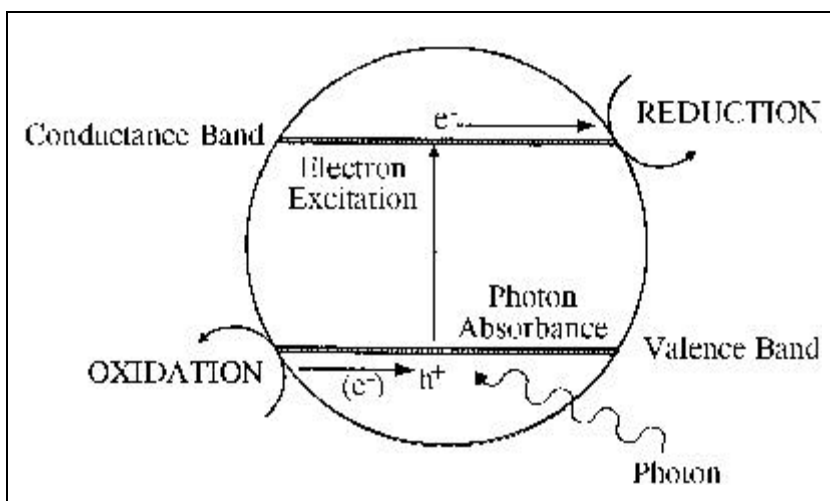


Figure 12. Schematic illustrating the basic process of photoassisted electron transfer reactions.

ACTIVITY IV, PROJECT 3A: PHOTOASSISTED ELECTRON TRANSFER REACTIONS FOR METAL-COMPLEXED CYANIDE

Project Overview

Previous research efforts under the MWTP for the remediation of mine wastewaters predominantly focused on removing toxic heavy metal cations from solution. This was accomplished with chemical processes that generated heavy-metal sludges that were then removed from the water stream by solid-liquid separation processes. However, many of the anions associated with the heavy metal cations in the wastewater are also toxic but remain in solution even after the sludge is generated and separated. Consequently, researchers at Montana Tech are examining processes to remediate the anions, particularly sulfur as sulfate, arsenic as arsenite and arsenate, nitrate, cyanide and metal-complexed cyanides. In this project, the remediation of metal-complexed cyanide is being investigated using several photolytic methods with the intent to identify and enhance naturally occurring remediation processes.

Overwhelming evidence shows that natural processes occur to heal environmental scars caused by mining activities. These processes

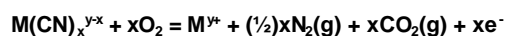
include electron-transfer reactions that lower the concentrations of the anionic mobile toxic constituents in surface and groundwaters through interactions with electromagnetic radiation (predominantly UV radiation but some visible light) from the sun. However, such direct natural photolytic processes suffer at night, on cloudy days, and in winter months. During these periods, artificial radiation sources are needed for sustainment. Furthermore, because the photolytic processes usually proceed slowly, catalysts are used to absorb the radiation and transfer the energy to the reactants to remediate the water within more acceptable timeframes. Such photocatalysts are either solid semiconductors (heterogeneous photocatalysts) or dissolved radicals in solution (homogeneous photosensitizers).

Technology Description

Background—When electromagnetic radiation is absorbed, electrons in the absorbing species pass from a singlet ground state (S_0) to an excited electronic

state (S_1) as shown in Figure 12. As long as the electron remains in the excited state, the absorbing species are more susceptible to their chemical environment and are therefore more apt to participate in electron-transfer reactions. The absorbing species undergo photoreduction when it donates the excited electron. Conversely, photooxidation occurs when the absorbing species accept an electron. In either case, the photoreduction and photooxidation reactions can lead to the destruction of the mobile toxic constituent.

For metal-complexed cyanide, only photooxidation can be used and in a reaction similar to cyanide photooxidation (see Project 3) where carbon dioxide and nitrogen gases are reaction products:



Clearly, solutions containing metal-complexed cyanides can also be rendered nontoxic through photolysis.

However, it is important to note that several competing processes may occur (see Figure 12) and must be prevented and/or minimized to maximize the efficiency of photoassisted electron transfer reactions. Furthermore, the photooxidation reaction becomes more difficult depending on the strength of the M-CN bonds. For this reason, the metal-complexed cyanides have been grouped as weak acid dissociables (WADs) and strong acid dissociables (SADs). In this regard, certain metal-complexed cyanides should be easy to photolytically remediate (copper and zinc) while others should be much more difficult (cobalt and gold).

Direct Photolysis—In this process, the mobile toxic constituent being remediated must absorb the electromagnetic radiation. Although this phenomenon is rare, it does occur with some metal-complexed cyanides but is dependent on the solution conditions. Research is being conducted to identify these conditions.

Homogeneous Photolysis—In this process, aqueous photosensitizers absorb the electromagnetic radiation and then transfer the photon energy to the mobile toxic constituents being remediated. Because the

process occurs in bulk solution, its kinetics are dependent on the solution conditions and the concentrations of the photosensitizers and the mobile toxic constituents. When the aqueous photosensitizer is not consumed during the process, it is referred to as homogeneous photocatalysis. In this regard, research is being conducted to identify the conditions needed for using either homogeneous photosensitizers or homogeneous photocatalysts for metal-complexed cyanide remediation.

Heterogeneous Photocatalysis—In this process, solid semiconductors are used to absorb the electromagnetic radiation and then transfer the photon energy to the mobile toxic constituent being remediated. However, electron transfer reactions can only occur if the mobile toxic constituent is adsorbed at the surface of the semiconductor. Thus, reaction kinetics are dependent on the mobile toxic constituent concentration as well as the rate of adsorption of the constituent, the available surface area of the semiconductor, and the rate of desorption of the reaction products. Consequently, reaction kinetics can be three orders of magnitude slower than reactions with homogeneous photolysis.

Nevertheless, reaction efficiencies are usually higher with heterogeneous photocatalysis due to the higher efficiency of photon capture and the increased "life" of the electron in the excited state. This is ultimately attributed to the properties of the semiconductor. With semiconductors, electrons are promoted from the valence band and into the conductance band across a band gap (Figure 13). The photon energy must be greater than or equal to the band gap energy. Excited electrons in the conductance band can then be donated to the mobile toxic constituent to induce its reduction. Likewise, the electron vacancy or "hole" in the valence band can accept electrons from the mobile toxic constituent and thereby induce its oxidation. The process is similar to the process described earlier (see Figure 12); however, it is evident that solution conditions must also be well-defined to control reactant adsorption and product desorption. In this regard, studies are being conducted to optimize these conditions for metal-complexed cyanide oxidation reactions. For now, only

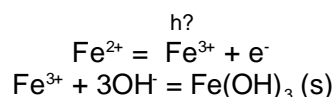
ACTIVITY IV, PROJECT 3B: PHOTOASSISTED ELECTRON TRANSFER REACTIONS FOR BERKELEY PIT WATER

Project Overview

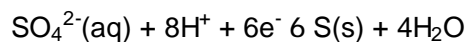
See Activity IV, Project 3A for Project Overview.

Technology Description

Background—When electromagnetic radiation is absorbed, electrons in the absorbing species pass from a singlet ground state (S_0) to an excited electronic state (S_1) as shown in Figure 12. As long as the electron remains in the excited state, the absorbing species are more susceptible to their chemical environment and are therefore more apt to participate in electron-transfer reactions. The absorbing species undergo photoreduction when it donates the excited electron. Conversely, photooxidation occurs when the absorbing species accept an electron. In either case, the photoreduction and photooxidation reactions can lead to the precipitation of mobile toxic constituents. For example, ferrous cations can be precipitated as ferri-hydroxide after being photooxidized to ferric cations:



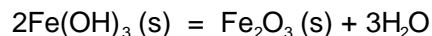
This reaction mechanism may account for the natural precipitation events observed in Berkeley Pit water. Once the iron is precipitated and separated, photolysis and/or conventional hydrometallurgical processes can then be used to recover the valuable mobile toxic constituents. On the other hand, a photoreduction reaction is exemplified by sulfate conversion to elemental sulfur:



Clearly, acid mine waters can be remediated through photolysis. However, it is important to note that several competing processes may occur (see Figure 12) and must be prevented

and/or minimized to maximize the efficiency of photoassisted electron transfer reactions.

Nevertheless, reaction efficiencies are usually higher with heterogeneous photocatalysis due to the higher efficiency of photon capture and the increased "life" of the electron in the excited state. This is ultimately attributed to the properties of the semiconductor. With semiconductors, electrons are promoted from the valence band and into the conductance band across a band gap (see Figure 13). The photon energy must be greater than or equal to the band gap energy. Excited electrons in the conductance band can then be donated to the mobile toxic constituent to induce its reduction. Likewise, the electron vacancy or "hole" in the valence band can accept electrons from the mobile toxic constituent and thereby induce its oxidation. The process is similar to the process described earlier (see Figure 12); however, it is evident that solution conditions must be well-defined to control reactant adsorption and product desorption. In this regard, studies are being conducted to optimize these conditions for metal-complexed cyanide oxidation reactions. For now, both hematite (Fe_2O_3) and anatase (TiO_2) are being investigated. Hematite is important because it can actually be formed by recycling the precipitated ferrihydrite



whereas the anatase is important because it has the highest known efficiency of semiconductors.

Status

The quality assurance project plan was written and is awaiting EPA approval. The final report should be completed by June 1997.

ACTIVITY IV, PROJECT 4: METAL ION REMOVAL FROM ACID MINE WASTEWATERS BY NEUTRAL CHELATING POLYMERS

Project Overview

A bench-scale research project is in progress at Montana Tech to eliminate or minimize some current economic or technical difficulties that exist in treatment technologies for acid mine wastewater. The novel technology is based on neutral chelating polymers that can have their chelating property turned on and off. The chelate switch will be based on known electrochemical or photochemical properties of electrically conducting polymers.

Technology Description

Chelates are chemical substances that have more than one binding site on the molecule; these added binding sites attach a molecule to a metal ion more strongly than a single binding site. The result is that chelates can be very effective at removing metal ions from wastewater. Chelates can be ionic or neutral. Ionic chelates exchange a cation (H^+ or Na^+) for the metal ion removed from the solution. Neutral chelates are electrically neutral and do not add material to the solutions when the metal ions are removed.

The removal of metal ions from aqueous solutions is presently accomplished by a variety of chemical and electrochemical processes. These techniques have distinct advantages in the appropriate situations (pH range, concentration range, matrix composition, etc.); however, they may not be practical under less-than-optimum operating conditions.

The goal of this project is to develop an alternate technology that requires no additional chemicals and that can produce

a marketable product, such as pure metals, and reduce costs and waste volume. The research project is a collaborative effort between academic and government resources, including the Haskell Indian Nations Universities' Haskell Environmental Research Studies Center. Initially, the project focus was on the design of chelating polymer systems for laboratory study and for theoretical study (molecular modeling). The first polymer systems were based on current literature information. Modeling results were compared to experimental and literature results as a means to test the validity of the theoretical data.

The validated modeling procedure was used to design and test a variety of neutral chelating systems for their capability to remove metal ions and associated anions from acid mine wastewater. The neutral chelating polymers determined to be most effective for water cleanup by the preliminary experimentation and the modeling studies were studied more thoroughly. The polymeric systems were evaluated for their removal efficiencies, contaminant capacity, ruggedness, ease of use, and cost effectiveness. Other important parameters identified in the preliminary studies were also used in the systems evaluations.

A more detailed process evaluation procedure was developed from the results of the refined experimentation. The selected polymeric system was then completely studied using a variety of synthetic and actual mine wastewater.

Status

All work for this project was completed. The final report has been written and is being reviewed.

ACTIVITY IV, PROJECT 5: REMOVAL OF ARSENIC AS STORABLE STABLE PRECIPITATES

Project Overview

The objective of this project is to strip arsenic from solutions in such a way as to produce

apatite mineral-like precipitated products that are stable for long-term storage in tailing pond environments. Substitution of arsenic into an apatite structure will provide a solid solution mineral compound that is environmentally stable for outdoor pond storage.

Technology Description

Earlier research demonstrated that a precipitation technique is effective in removing arsenic (to low micrograms/liter concentrations) from aqueous solutions (EPA-supported project). The precipitation is conducted in a way to form a solid solution compound containing arsenate and phosphate in an apatite mineral-like phase. This solid is stable to the EPA's Toxicity Characteristic Leaching Procedure (TCLP), and more importantly, the solubility is one to two orders of magnitude less than calcium arsenate in aqueous solutions over the pH range of 9 to 12 (the range of pH values maintained in tailing ponds).

In the early 1980s, it was demonstrated that lime precipitation of calcium arsenate with subsequent storage in a tailings pond environment is unacceptable because at pH levels above approximately 8.5, calcium arsenate will be converted to calcium carbonate (by carbon dioxide in air) with the release of arsenic into the aqueous phase. Removal of arsenic by precipitation as calcium arsenate has been discontinued by industry and has been replaced by ferric arsenate precipitation (EPA's Best Demonstrated Available Technology for arsenic-bearing solutions). However, even though low concentrations of arsenic in solutions can be achieved by ferric precipitation, it has been demonstrated that the removal from solution is actually an adsorption phenomena. Therefore, long-term stability of such residues in tailings pond environments may not be appropriate, hence the need for the present study.

Stability of Mineral-Like

Residues—Montana Tech researcher's approach to arsenic storage was to form a mineral-like phase that shows equilibrium-phase stability under tailings pond

environmental conditions. If equilibrium-phase stability is achieved (for a given environment), then long-term stability would be ensured (at least for as long as the environmental conditions are maintained). This project is supporting an intensive investigation of the formation of arsenic precipitates in two systems, i.e., the calcium-arsenic-phosphate (apatite-like solid solutions of arsenate and phosphate) system, and the ferric-arsenic-phosphate (phosphoscorodite-like solid solutions of arsenate and phosphate) system. Both of these systems show great promise for industrial application, if long-term stability can be demonstrated.

Status

The initial phase was completed. Long-term stability tests were performed, and data from these tests is being evaluated. The project will be completed in May 1997.

An extension of the project is expected in the spring of 1997.

The precipitation "recipe" was applied to two industrially contaminated waters, and the long-term stability of the resulting products will be tested. Successful demonstrations will result in a new way to treat arsenic-bearing wastewaters and mine drainage solutions.

ACTIVITY IV PROJECT 7: BERKELEY PIT INNOVATIVE TECHNOLOGIES PROJECT

Project Overview

The purpose of the Berkeley Pit Innovative Technologies Project is to provide a test bed for high risk/innovative technologies for the remediation of Berkeley Pit water. The project is focused on bench-scale testing of remediation technologies to help assist in defining alternative remediation strategies for the EPA's future cleanup objectives for Berkeley Pit waters.

The project will focus on bench-scale testing of innovative technologies for treating the water flowing into and existing in the Berkeley Pit. Individuals, companies, or academic institutions with existing remediation technologies are invited to demonstrate their process for the project and write a report summarizing their process and the results of their bench-scale test. A copy of the report from each test will be forwarded for evaluation by the EPA Region VIII field office, the EPA NRMRL, and the DOE Resource Recovery Project, also implemented by MSE.

The project seeks subcontractors to perform bench-scale tests of innovative remediation technologies for water flowing into or existing in the Berkeley Pit. Ideally, the subcontractor's process will treat Berkeley Pit water to produce water of sufficient quality that it can be discharged with no further treatment and a small quantity of relatively stable residue containing highly concentrated amounts of the elements and compounds found in the Berkeley Pit.

Avenue for Participation

Option 1: Funded Testing at Montana Tech

Montana Tech will provide water from the Berkeley Pit and will store and dispense water from the bench-scale tests. Montana Tech has also provided a laboratory to be used for the remediation testing.

Quality control during the demonstration tests is essential. Before beginning bench-scale tests at Montana Tech, a quality assurance project plan must be developed in sufficient detail to demonstrate that the intended measurements are appropriate for achieving project objectives, quality control procedures are sufficient for obtaining data of known and adequate quality, and such data will be defensible if challenged technically.

Upon completion of bench-scale tests and before leaving Montana Tech, the subcontractor will be required to write an exit report with supporting data tables, summarizing the process and results of the bench-scale tests.

Option 2: Funded Testing Off Site

Montana Tech will facilitate delivery of Berkeley Pit water to the subcontractor's site. Quality control during the demonstration tests is essential, and the quality assurance project plan must be submitted and approved before any water will be shipped. The subcontractor must also satisfy project personnel that proper hazardous waste and safety programs are in place at their site.

Upon completion of off-site bench-scale tests, the subcontractor will be required to write and submit a final report with supporting data tables, summarizing the process and results of the bench-scale tests.

Option 3: Unfunded Alternative Avenues for Participation

Participation at Montana Tech—There may be potential researchers who are willing to bring their technology to the project laboratory under their own financial support. The Project Manager for the Berkeley Pit Innovative Technologies Project and the Project Manager for MWTP Activities from Montana Tech will review each technology that may be presented under this avenue on a case-by-case basis for testing at any time. Potential unfunded participants are encouraged to contact the project managers to initiate discussion before submitting a proposal.

Off-Site Participation—The Berkeley Pit Innovative Technologies Project has a mechanism in place to ship water to credible researchers. Berkeley Pit water will be on hand for shipping from the project laboratory to facilitate the work of other researchers. The requirements for the project to ship water are that the investigators:

- can demonstrate their work will contribute to the investigation of solutions to the remediation of Berkeley Pit waters;
- will return a timely report to the project on the results of their research;
- can demonstrate they have satisfactory hazardous materials handling and disposal capabilities; and
- have an adequate safety plan.

Status

Three funded and one unfunded technology providers performed bench-scale technology demonstrations at Montana Tech. A fifth technology provider will demonstrate in October of 1996. Final reports from all completed demonstrations are currently being reviewed.

A new Request for Proposals is expected to be made available in January 1997. Funded proposal requests are due by February 1997.

TECHNOLOGY TRANSFER ACTIVITY V OVERVIEW

This activity consists of making technical information developed during MWTP activities available to industry, academia, and Government agencies. Tasks include preparing and distributing MWTP reports, presenting information about the MWTP to various groups, holding Interagency Agreement Management Committee meetings, sponsoring mine waste conferences, and working to commercialize treatment technologies.

Fiscal Year 1996 Highlights

- The 1995 MWTP Annual Report was published. This report explains the MWTP and summarizes accomplishments for FY95. A similar report will be published each year.
- Several MWTP professionals appeared at varied meetings to discuss the Program with interested parties. Many mine waste conferences, as well as mining industry meetings, were attended.
- Investigations were conducted on how best to integrate and interface with the ongoing technology transfer activities of the Federal Government.
- Activity I, Volume 6, Pyrite, was completed.

TRAINING AND EDUCATION ACTIVITY VI OVERVIEW

Through its education and training programs, the MWTP continues to educate professionals and the general public about the latest information regarding mine and mineral waste cleanup methods and research. This effort is being directed by the Professor of Mining Engineering at Montana Tech.

As a result of rapid technology and regulatory changes, professionals working in the mine- and mineral-waste areas often encounter difficulties in upgrading their knowledge and skills in these fields. Only in recent years have environmental issues related to the mining and mineral industries received widespread public, industry, and political attention. While knowledge of current research and technology is vital for dealing with mine and mineral wastes, time and costs may prevent companies from sending employees back to the college classroom.

Through short courses, workshops, conferences, and video outreach, Activity VI of the MWTP educates professionals and the general public and brings the specific information being generated by bench-scale research and pilot-scale technologies to those who work in mine- and mineral-waste remediation.

Fiscal Year 1996 Highlights

- The *Mine Design, Operations, and Closure Conference '96*, conducted in March 1996, continued last year's interagency cooperation. The 5-day event was cosponsored by the U.S. Forest Service; U.S. Bureau of Land Management; Montana Department of State Lands; MSE; Haskell Environmental Research Studies Center; Salish-Kootenai College; several other private companies; and Montana Tech. During the conference, experts presented overviews on such topics as predictive chemical modeling for acid mine drainage, mine water quality source control, state-of-the-art containment technologies, and innovative pit reclamation. Over 150 mine operators, consultants, and professionals from the private and public sectors attended the conference.
- The Mine and Mineral Waste Emphasis Program now has an enrollment of 8 students, with all of them receiving funding from the MWTP. This is an interdisciplinary graduate program that allows students to major in their choice of a wide variety of technical disciplines while maintaining an emphasis in mining and mineral waste.
- The MWTP supported Teachers' Enhancement and a kindergarten through grade 12 program, which provides educational materials regarding the production, handling, and processing of mine wastes.
- A group of Mine and Mineral Waste Emphasis graduate students attended the *Mine Design, Operations, and Closure Conference '96*.
- A cooperative agreement is in place for work with the Haskell Environmental Research Studies Center at Haskell Indian Nations University.
- Graduate students in the Mine and Mineral Waste Emphasis Program are working on projects in Activities III and IV.

- The Mine and Mineral Waste Emphasis Program continued to offer the courses, *MWTP Field Demonstrations* and *MWTP Bench-Scale Research*. These courses acquainted the Mine and Mineral Waste Emphasis Program students to the other activities of the MWTP.

Future Activities

The following training and education activities are scheduled for the first part of 1997:

- The MWTP Training and Educational activities will offer the *Mine Design, Operations, and Closure Conference '97* in April 1997. In addition to last year's interagency sponsors, it is hoped that more private-sector sponsors can be added.
- The MWTP is working on a cooperative education package for the U.S. Forest Service.
- All funded Mine and Mineral Waste Emphasis Program graduate students will work on mine waste-oriented projects as a part of their funding requirements.

FINANCIAL SUMMARY

Total expenditures during the period October 1, 1995, through September 30, 1996, were \$2,890,832, including both labor and non-labor expense categories. All costs incurred after September 30, 1996, will be included in the Fiscal 1997 Annual Report.

The cumulative authorized budget for the period was \$3,100,000.

Individual activity accounts are depicted on the performance graph (Figure 14).

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